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CLAIMS

[Claim(s)]

[Claim 1] a) The process which prepares the ink jet record element which changes including the base material which has upwards the porous image acceptance layer which has the continuous void, And it is the ink jet printing approach for raising the ozone stability of the ink jet image which has the process which applies the globule of water, a moisturizer, and the liquid ink containing metalization phthalocyanine dye to the image on the b aforementioned image acceptance layer. The ink-jet printing approach that said metalization phthalocyanine dye has a degree type: MPc(SO₃X) a(SO₂NRR') b (M among an upper type) It is a metal and Pc is a phthalocyanine nucleus. X They are hydrogen, alkali metal, or an organic cation. a It is 0-2 and R is the permutation of hydrogen and carbon numbers 1-15 or an unsubstituted alkyl group, a permutation, an unsubstituted aryl group, a permutation, or an unsubstituted heterocycle type machine. R' Although it is the permutation or the unsubstituted heterocycle type machine which has the permutation which has the permutation of the carbon numbers 1-15 which have a hydroxy group or an unsubstituted alkyl group, and a hydroxy group, an unsubstituted aryl group, or a hydroxy group and b is 1-4 a+b averages and it is 3-4.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]**[0001]**

[Field of the Invention] This invention relates to the ink jet printing approach which raises the ozone stability of an ink jet image.

[0002]

[Description of the Prior Art] Ink jet printing is the non impact approach which forms an image by answering a digital signal and making a liquid ink drop adhere to an image recording element in the format for every pixel. Adhesion of the liquid ink drop to an image recording element top is controlled, and the various approaches of using for generating a desired image exist. Although one process is known as a continuous ink jet, the continuation stream of a drop is electrified and the image is deflected to up to the front face of an image recording element, the drop by which image formation is not carried out is caught and is returned to ink **. Another process is known as a drop ink jet on demand, when required, it emits each liquid ink drop on an image recording element, and it forms a desired image. A piezoelectric transducer and heat bubble formation are included in the general approach of controlling emission of a liquid ink drop by drop printing on demand. The ink jet printer has the wide range application covering the market of the range of little printing of an office document, and pictorial image formation from industrial use labeling.

[0003] The ink used for various ink jet printers is classified into a pigment system or a pigment system. Coloring matter is a color material dissolved in a carrier medium. A carrier medium can turn into a liquid or a solid-state at a room temperature. Usually, the mixture of water or water, and an organic auxiliary solvent is contained in the carrier medium used. Each coloring matter molecule is surrounded with the molecule of a carrier medium. In the case of pigment system ink, there is no particle seen under a microscope. although the advance latest [many] is seen in the technical field of pigment system ink jet ink, still more, such ink is low optical density in a regular paper, and is inferior in lightfastness — like — it has the fault. When using water as a carrier medium, generally such ink also has the fault that a water resisting property is also inferior.

[0004] When the short-time pan of the ink jet acceptance element which can use the above-mentioned ink is carried out to water, it must suit some requirements including generating a smear (smear), bleeding, or the high concentration image that does not carry out a wander (wander).

[0005] the [U.S. Pat. No. 4,632,703, 6,149,722 and 6,015,896, and international public presentation official report WO 00/No. 08103 said] — WO 98/No. 4923 is related with the ink containing the phthalocyanine dye used for ink jet printing. However, publication of being useful does not have these ink in these reference about the record element which has a porous image acceptance layer.

[0006]

[Problem(s) to be Solved by the Invention] It is the purpose of this invention to offer the ink jet printing approach which raises the ozone stability of an ink jet image.

[0007]

[Means for Solving the Problem] The above-mentioned purpose a continuation The process which prepares the ink jet record element which changes including the base material which has

the porous image acceptance layer which has the void carried out upwards, And it is the ink jet printing approach for raising the ozone stability of the ink jet image which has the process which applies the globule of water, a moisturizer, and the liquid ink containing metalization phthalocyanine dye to the image on the b aforementioned image acceptance layer. said metalization phthalocyanine dye — degree type: — MPc(SO₃X) _a(SO₂NRR') _b (M among an upper type) It is a metal and Pc is a phthalocyanine nucleus. X They are hydrogen, alkali metal, or an organic cation. a It is 0—2 and R is the permutation of hydrogen and carbon numbers 1—15 or an unsubstituted alkyl group, a permutation, an unsubstituted aryl group, a permutation, or an unsubstituted heterocycle type machine. R' Although it is the permutation or the unsubstituted heterocycle type machine which has the permutation which has the permutation of the carbon numbers 1—15 which have a hydroxy group or an unsubstituted alkyl group, and a hydroxy group, an unsubstituted aryl group, or a hydroxy group and b is 1—4 a+b — averaging — 3—4 — it is — it attains according to this invention which offers the ink jet printing approach which it has. When the above-mentioned compound was used, the ozone stability of an ink jet image improved.

[0008]

[Embodiment of the Invention] : by which the following are contained in the metalization phthalocyanine dye which can be used in the desirable mode of this invention [0009]

[Table 1]



(MはCuであり、そしてX、Pc、a及びbは前出の通りである)

表 I

| 色素 | R' |
|----|-------------------------------------|
| 1 | |
| 2 | |
| 3 | |
| 4 | -CH ₂ CH ₂ OH |

[0010]

[Table 2]



(R=R' =-CH₂CH₂OH、そしてX、Pc、a及びbは前出の通りである)

表 II

| 色素 | M |
|----|----|
| 5 | Cu |
| 6 | Ni |

[0011] In another desirable mode of this invention, R is a heterocycle type substituent which has

the aryl group or hydroxy group which has the permutation of the carbon numbers 1–15 which have a hydroxy group or an unsubstituted alkyl group, and a hydroxy group.

[0012] The above-mentioned coloring matter can be used in any amount effective in the meant purpose. Generally, the good result was obtained when coloring matter existed in the amount of 0.3 – 3 mass % preferably, 0.2 to 5 mass [of an ink jet ink constituent] %, and. Moreover, coloring matter mixture can also be used.

[0013] That by which the base material of the ink jet record element used for this invention is usually used for an ink jet acceptor, For example, plastics, such as polyester type resin like paper, resin coat paper, and polyethylene terephthalate, Polycarbonate resin, polysulfone resin, methacrylic resin, cellophane, Acetate plastics, diacetyl cellulose, a cellulose triacetate, vinyl chloride resin, Polyethylene naphthalene, 2 acetic-acid polyester, various glass ingredients, The micro void polyester indicated by the list at the United States patent application/[09th] No. 656,129 (August 29, 2000 application) specification, a trade name Teslin (trademark) (PPG Industries, Inc., and Pittsburgh —) The polyethylene polymer content ingredient currently sold in Pennsylvania, A Tyvek (trademark) synthetic paper (DuPont Corp.), And it can become other complex films which are indicated by fine foam lists, such as an Oppalyte (trademark) film (Mobil Chemical Co.), at the U.S. Pat. No. 5,244,861 specification. The base material used for this invention can have preferably 12–500 micrometers of thickness of 75–300 micrometers, for example.

[0014] As long as it is required, an antioxidant, an antistatic agent, a plasticizer, and other known additives may be introduced into a base material. Paper is used in a desirable mode.

[0015] In the desirable mode of this invention, a porous ink absorbing layer contains inorganic particles, such as a silica, an alumina, a titanium dioxide, clay, a calcium carbonate, a barium sulfate, or a zinc oxide. In another desirable mode, a porous ink absorbing layer contains 30% – 95% of inorganic particles, and polymer binder (for example, gelatin, polyvinyl alcohol, polyvinyl pyrrolidinone, or polyvinyl acetate) 5%–70%. Moreover, a porous ink absorbing layer can also have the polymer microporous structure which does not contain an inorganic filler particle as had an organic bead or shown in U.S. Pat. No. 5,374,475 and a 4,954,395 specification.

[0016] Polyvinyl alcohol, a polyvinyl pyrrolidone, poly ethyl oxazoline, the bone gelatin of Type IV which is deionized or is not deionized, acid-treatment ossein gelatin, or pig skin gelatin is contained in the example of the binder which can be used for an image acceptance layer, a hydrophilic polymer — 0.4–30g/m² — it can exist in the amount of 1 – 16 g/m² preferably.

[0017] pH of the water-color-ink constituent of this invention can be adjusted by adding organic or inorganic an acid or a base. Useful ink can have desirable pH of 2–7 depending on the class of coloring matter to be used. A hydrochloric acid, a phosphoric acid, and a sulfuric acid are contained in a typical inorganic acid. Methansulfonic acid, an acetic acid, and a lactic acid are contained in a typical organic acid. An alkali-metal hydroxide and a carbonate are contained in a typical inorganic base. Ammonia, triethanolamine, and tetramethylethylenediamine are contained in a typical organic base.

[0018] A moisturizer is used for the ink jet ink constituent of this invention in order to prevent ink drying within the orifice of a print head, or solidifying and attaching. For the example of the moisturizer which can be used polyhydric alcohol, for example, ethylene glycol, A diethylene glycol, triethylene glycol, propylene glycol, Tetraethylene glycol, a polyethylene glycol, glycerol, The 2-methyl –2, 4-pentanediol, 1 and 2, 6-hexane triol, and a thioglycol; The low-grade alkyl monochrome or diether guided from alkylene glycol, For example, ethylene glucohol monomethyl or the monoethyl ether, diethylene-glycol monomethyl, or the monoethyl ether, Propylene glycol monomethyl or the monoethyl ether, triethylene glycol monomethyl, or the monoethyl ether, Diethylene-glycol dimethyl or diethylether, and the diethylene-glycol monobutyl ether; A nitrogen content ring compound, For example, a pyrrolidone, a N-methyl-2-pyrrolidone, and 1,3-dimethyl-2-imidazolidinone; a sulfur content compound, for example, dimethyl sulfoxide, and a tetramethylen sulfone are contained in a list. A moisturizer desirable to the constituent of this invention is a diethylene glycol, glycerol, or the diethylene-glycol monobutyl ether.

[0019] When an acceptor object, especially a base are altitude size papers, in order to help ink osmosis, a water miscibility organic solvent may be added to the water color ink of this invention.

For the example of such a solvent alcohols, for example, methyl alcohol, Ethyl alcohol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, sec-butyl alcohol, t-butyl alcohol, Isobutyl alcohol, furfuryl alcohol, and tetrahydrofurfuryl alcohol; Ketones or keto alcohol For example, an acetone, a methyl ethyl ketone, diacetone alcohol; ether, for example, a tetrahydrofuran, and dioxane; ester, for example, ethyl lactate, ethylene carbonate, and propylene carbonate are contained in a list.

[0020] A surface active agent may be added and the surface tension of the ink to paper may be adjusted on suitable level. A surface active agent can serve as anionic, cationicity, both sexes, or nonionic. A surfactant desirable to the ink constituent of this invention is 0.1% – 1.0% of Surfynols by the last concentration (product made from Air Products (trademark)).

[0021] Microorganism [the microorganism in the inside of water color ink], for example, in order to mold and to control growth of true fungi, a destruction-of-life agent may be added to the constituent of this invention. A destruction-of-life agent desirable to the ink constituent of this invention is Proxel(trademark) GXL (Zeneca Specialties Co.) of the last concentration 0.05 – 0.5 mass %.

[0022] The typical ink constituent of this invention is :color material (0.2 – 5%) which can become the following (mass criteria), water (20 – 95%), a moisturizer (5 – 70%), a water miscibility auxiliary solvent (2 – 20%), a surfactant (0.1 – 10%), a destruction-of-life agent (0.05 – 5%), and a pH regulator (0.1 – 10%).

[0023] A thickener, a conductive reinforcement, a KOGESHON inhibitor, a drying agent, and a defoaming agent are contained in the additive of the addition which can exist optionally alternatively in the ink jet ink constituent of this invention.

[0024] The image recording layer used for the record element of this invention In order to contribute to the property of the record element used for this invention of not blocking and to control those resistance to contamination, A flatting, for example, a titanium dioxide, a zinc oxide, a silica, and a polymer bead (for example, bridge formation polymethylmethacrylate or polystyrene beads); In order to improve ink absorptivity resin or the aging behavior of a layer, In order to raise the surface homogeneity of an ink absorbing layer there for the promotion of absorption of ink by which continuation application is carried out, and desiccation, And the surfactant for adjusting the surface tension of desiccation coating, For example, nonionic, a hydrocarbon, a carbon fluoride surface active agent, or a cationic surface active agent (For example, quarternary ammonium salt); — fluorochrome; — pH control agent; — defoaming agent; — lubricant; — antiseptics; — viscous amelioration agent; — coloring matter fixing agent; — waterproofing agent; — dispersant; — UV absorbent; — antifungal agent; — mordant; — antistatic-agent; — antioxidant; — a fluorescent brightener — The various known additives containing ** can also be contained. If required, a hardening agent can also be added to an ink absorbing layer.

[0025] In order to improve the adhesive property of the image recording layer to a base material, before applying an image recording layer, a support surface may be applied to processing of corona discharge treatment etc. Furthermore, under-coating layers, such as a layer formed from a halogenation phenol or the vinyl chloride-vinyl acetate copolymer hydrolyzed partially, can be applied to a support surface, and the adhesive property of an image recording layer can be raised. When using an under-coating layer, as for the thickness, it is good that it is less than (desiccation coat thickness) 2 micrometers.

[0026] An image recording layer can exist in any amount effective in the purpose to mean. general — 2 – 46 g/m² — the good result is obtained if it exists preferably in the amount of 6 – 16 g/m² (respectively — 2-42 micrometers — desirable — the thickness of 6-15 micrometers – – corresponding).

[0027]

[Example] Practicality of this invention is clarified by the following examples.

:temperature which prepared the compound 2 of the synthetic above-mentioned of a compound 2 as follows was maintained below 40 degrees C, and the copper phthalocyanine (14g) was added to the chlorosulfonic acid (125g) over 45 minutes. And it heated at 140 degrees C – 150 degrees C of this mixture, and stirred for 5 hours. After cooling to a room temperature, the thionyl

chloride (49g) was dropped over 30 minutes, and this mixture was maintained at 80 degrees C for 3 hours. After cooling to a room temperature, Hikami was filled with this mixture, it stirred with sufficient vigor, and temperature was maintained below 5 degrees C. Precipitate was carried out the ** exception, a lot of water washed at 5 degrees C, and it used at the following process. N and N-screw (hydroxyethyl) trimethylene diamine (27g) and a sodium carbonate (15g) were dissolved in water 500mL at 5 degrees C. The damp phthalocyanine filter cake was all added at once, and this reaction mixture was warmed to the room temperature, and was heated at 50 degrees C after that overnight. Ethanol (1.5L) was added and most organic substances were carried out the ** exception. Condensed the mixed liquor object, and it was made to deposit with an acetone, and carried out the ** exception, and the compound 2 was generated when it was made to wash and dry by ethanol. Other compounds and nickel analogs in Table I were also prepared similarly.

[0028] Example 1: copper-phthalocyanine coloring matter record element 1 fumed alumina (Cab-O-Sperse(trademark) PG003, Cabot Corp.), polyvinyl alcohol (Gohsenol(trademark) GH-23A, Nippon Gohsei Co., Ltd.) and 2, and 3-dihydroxy-1,4-dioxane (Clariant Corp.) was mixed by the ratio of 88:10:2, the aquosity coating formulation of 30 mass % solid content was obtained, and the coating solution for base layers was prepared. Fumed alumina (Cab-O-Sperse(trademark) PG003), polyvinyl alcohol (Gohsenol(trademark) GH-23A), and Polymer A were mixed by the ratio of 85:3:12, the aquosity coating formulation of 10 mass % solid content was obtained, and the coating solution for image acceptance layers was prepared. Polymer A is N-vinylbenzyl. – It is a mordant polymer containing the polymer particle which consists of N, N, and N-trimethyl ammonium-chloride 87 mass % and divinylbenzene 13 mass %. A fumed alumina particle has primary particle size with a diameter of 7~40nm, and is condensing it to a maximum of 150nm. Little addition of surfactant Zonyl(trademark) FSN (E. Idu Pont de Nemours and Co.) and Olin (trademark)10G (Dixie chemical Co.) was carried out as a spreading assistant.

[0029] The bead coat of the above-mentioned coating solution was carried out to coincidence at 40 degrees C on the polyethylene coat paper base beforehand covered over corona discharge treatment. The coat of the image acceptance layer was carried out to the topmost part of a base layer. And this coating was dried at 60 degrees C by forced air, and the two-layer record element whose thickness of a bottom member and a topmost part layer is 40 micrometers (43 g/m²) and 2 micrometers (2.2 g/m²), respectively was produced.

[0030] : using the acceptance element of marketing of the following equipped with the record element 2 porosity image acceptance layer — Konica Photo Quality Ink Jet Paper Qp and No.KJP-LT-GH-15-QP PI.

[0031] It prepared using the deionized water which does a moisturizer, a diethylene glycol, and glycerol for the ink containing the coloring matter used for this invention of the preparation above-mentioned of ink, and ink given in Table III, and does 0.5 mass % content of 0.003 mass % and a surfactant, and Surfynol 465 (trademark) (Air Products Co.) for six mass each %, a destruction-of-life agent, and ProxelGXL (trademark). These coloring matter concentrates were based on the solution absorption spectrum, and the last ink chose them so that the vitrification optical density of about 1.0 might be produced (when 1:1000 dilutes).

[0032] Although it was preparation metalization phthalocyanine dye of contrast ink, these ink as well as the ink of this invention was prepared except having used the following contrast coloring matter which has a different substituent from the above-mentioned thing of this invention.

C-1: direct — c is 2~4 in blue (Direct Blue) 199C-2:CuPc(SO₃Na) a(SO₂NH(CH₂)₃SO₃Na) bC-3:CuPc(SO₃Na) c and here.

(Pc and a are the same as what was specified by the above-mentioned formula)

[0033] The printing above-mentioned ink of a test image was filtered through 0.45-micrometer polytetrafluoroethylene filter, it put into empty Lexmark ink cartridge No.Lexmark 15MO120, and the ink station of Lexmark Z-51 printer was equipped. It consisted of four kinds of concentration patch magnitude of about 10x10mm, and the test image which is the range of the dot covering range of 25% ~ 100% was printed to the above-mentioned element 1 and Konica Photo Quality Ink Jet Paper QP, and No.KJP-LT-GH-15-QP PI.

[0034] About evaluation each ink of a test image, the status A red reflection density of the

above-mentioned patch corresponding to 75% and 100% dot covering was measured using X-Rite (trademark) 820 densitometer. The red concentration of dot covering (D-max) is shown in Table III 100%. And the step image was placed for three days into the dark chamber which contains air and ozone gas 5ppm at 50% of relative humidity. The status A concentration of this step image was measured again, and the status A red concentration coloring matter retention in 75% dot covering patch was calculated about each ink. This also shows in Table III. It is thought that bigger retention than 45% can be admitted.

[0035]

[Table 3]

表III

| 色素含有インク | オゾン褪色保持率 (%) | |
|---------|--------------|--------|
| | 記録要素 1 | 記録要素 2 |
| 1 | 93 | 87 |
| 2 | 94 | 82 |
| 3 | 80 | NA |
| 4 | 92 | NA |
| 5 | 93 | 84 |
| C-1 | 24 | 23 |
| C-2 | 20 | 18 |
| C-3 | 20 | 19 |

[0036] The above-mentioned result shows that had less tenebrescence than contrast coloring matter in an ozone test, when the metalization phthalocyanine dye of this invention and a porous image acceptance layer are combined.

[0037] Example 2: this ink as well as the ink of this invention in Example 1 was prepared except having contained the preparation coloring matter 6 of the ink of nickel phthalocyanine dye this invention.

These ink as well as the ink of this invention was prepared except having used the following contrast coloring matter which has a different substituent from the above-mentioned thing of preparation this invention of contrast ink. C-4: A nickel (II) phthalocyanine tetra-sulfonic acid, 4 sodium salt (Aldrich Chemical Co.).

[0038] The above-mentioned ink was printed and evaluated like Example 1 only using printing of a test image, and the evaluation record element 1. The following result was obtained.

[0039]

[Table 4]

表IV

| 色素含有インク | オゾン褪色保持率 (%) |
|---------|--------------|
| 6 | 100 |
| C-4 | 44 |

[0040] The above-mentioned result shows that there was no tenebrescence in an ozone test as compared with contrast coloring matter, when the metalization phthalocyanine dye of this invention and a porous image acceptance layer are combined.

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TECHNICAL FIELD

[Field of the Invention] This invention relates to the ink jet printing approach which raises the ozone stability of an ink jet image.

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TECHNICAL PROBLEM

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MEANS

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[0008]

[Embodiment of the Invention] : by which the following are contained in the metalization phthalocyanine dye which can be used in the desirable mode of this invention [0009]

[Table 1]



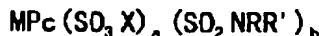
(MはCuであり、そしてX、Pc、a及びbは前出の通りである)

表 I

| 色素 | R' |
|----|----|
| 1 | |
| 2 | |
| 3 | |
| 4 | |

[0010]

[Table 2]



(R=R' = -CH₂CH₂OH、そしてX、Pc、a及びbは前出の通りである)

表Ⅱ

| 色素 | M |
|----|----|
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[0011] In another desirable mode of this invention, R is a heterocycle type substituent which has the aryl group or hydroxy group which has the permutation of the carbon numbers 1–15 which have a hydroxy group or an unsubstituted alkyl group, and a hydroxy group.

[0012] The above-mentioned coloring matter can be used in any amount effective in the meant purpose. Generally, the good result was obtained when coloring matter existed in the amount of 0.3 – 3 mass % preferably, 0.2 to 5 mass [% of an ink jet ink constituent], and. Moreover, coloring matter mixture can also be used.

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[0015] In the desirable mode of this invention, a porous ink absorbing layer contains inorganic particles, such as a silica, an alumina, a titanium dioxide, clay, a calcium carbonate, a barium sulfate, or a zinc oxide. In another desirable mode, a porous ink absorbing layer contains 30% – 95% of inorganic particles, and polymer binder (for example, gelatin, polyvinyl alcohol, polyvinyl pyrrolidinone, or polyvinyl acetate) 5%–70%. Moreover, a porous ink absorbing layer can also have the polymer microporous structure which does not contain an inorganic filler particle as had an organic bead or shown in U.S. Pat. No. 5,374,475 and a 4,954,395 specification.

[0016] Polyvinyl alcohol, a polyvinyl pyrrolidone, poly ethyl oxazoline, the bone gelatin of Type IV which is deionized or is not deionized, acid-treatment ossein gelatin, or pig skin gelatin is contained in the example of the binder which can be used for an image acceptance layer. a hydrophilic polymer — 0.4–30g/m² — it can exist in the amount of 1 – 16 g/m² preferably.

[0017] pH of the water-color-ink constituent of this invention can be adjusted by adding organic or inorganic an acid or a base. Useful ink can have desirable pH of 2–7 depending on the class of coloring matter to be used. A hydrochloric acid, a phosphoric acid, and a sulfuric acid are contained in a typical inorganic acid. Methansulfonic acid, an acetic acid, and a lactic acid are contained in a typical organic acid. An alkali-metal hydroxide and a carbonate are contained in a typical inorganic base. Ammonia, triethanolamine, and tetramethylethylenediamine are contained

in a typical organic base.

[0018] A moisturizer is used for the ink jet ink constituent of this invention in order to prevent ink drying within the orifice of a print head, or solidifying and attaching. For the example of the moisturizer which can be used polyhydric alcohol, for example, ethylene glycol, A diethylene glycol, triethylene glycol, propylene glycol, Tetraethylene glycol, a polyethylene glycol, glycerol, The 2-methyl -2, 4-pentanediol, 1 and 2, 6-hexane triol, and a thioglycol; The low-grade alkyl monochrome or diether guided from alkylene glycol, For example, ethylene glucohol monomethyl or the monoethyl ether, diethylene-glycol monomethyl, or the monoethyl ether, Propylene glycol monomethyl or the monoethyl ether, triethylene glycol monomethyl, or the monoethyl ether, Diethylene-glycol dimethyl or diethylether, and the diethylene-glycol monobutyl ether; A nitrogen content ring compound, For example, a pyrrolidone, a N-methyl-2-pyrrolidone, and 1,3-dimethyl-2-imidazolidinone; a sulfur content compound, for example, dimethyl sulfoxide, and a tetramethylen sulfone are contained in a list. A moisturizer desirable to the constituent of this invention is a diethylene glycol, glycerol, or the diethylene-glycol monobutyl ether.

[0019] When an acceptor object, especially a base are altitude size papers, in order to help ink osmosis, a water miscibility organic solvent may be added to the water color ink of this invention. For the example of such a solvent alcohols, for example, methyl alcohol, Ethyl alcohol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, sec-butyl alcohol, t-butyl alcohol, Isobutyl alcohol, furfuryl alcohol, and tetrahydrofurfuryl alcohol; Ketones or keto alcohol For example, an acetone, a methyl ethyl ketone, diacetone alcohol; ether, for example, a tetrahydrofuran, and dioxane; ester, for example, ethyl lactate, ethylene carbonate, and propylene carbonate are contained in a list.

[0020] A surface active agent may be added and the surface tension of the ink to paper may be adjusted on suitable level. A surface active agent can serve as anionic, cationicity, both sexes, or nonionic. A surfactant desirable to the ink constituent of this invention is 0.1% – 1.0% of Surfynols by the last concentration (product made from Air Products (trademark)).

[0021] Microorganism [the microorganism in the inside of water color ink], for example, in order to mold and to control growth of true fungi, a destruction-of-life agent may be added to the constituent of this invention. A destruction-of-life agent desirable to the ink constituent of this invention is Proxel(trademark) GXL (Zeneca Specialties Co.) of the last concentration 0.05 – 0.5 mass %.

[0022] The typical ink constituent of this invention is :color material (0.2 – 5%) which can become the following (mass criteria), water (20 – 95%), a moisturizer (5 – 70%), a water miscibility auxiliary solvent (2 – 20%), a surfactant (0.1 – 10%), a destruction-of-life agent (0.05 – 5%), and a pH regulator (0.1 – 10%).

[0023] A thickener, a conductive reinforcement, a KOGESHON inhibitor, a drying agent, and a defoaming agent are contained in the additive of the addition which can exist optionally alternatively in the ink jet ink constituent of this invention.

[0024] The image recording layer used for the record element of this invention In order to contribute to the property of the record element used for this invention of not blocking and to control those resistance to contamination, A flattening, for example, a titanium dioxide, a zinc oxide, a silica, and a polymer bead (for example, bridge formation polymethylmethacrylate or polystyrene beads); In order to improve ink absorptivity resin or the aging behavior of a layer, In order to raise the surface homogeneity of an ink absorbing layer there for the promotion of absorption of ink by which continuation application is carried out, and desiccation, And the surfactant for adjusting the surface tension of desiccation coating, For example, nonionic, a hydrocarbon, a carbon fluoride surface active agent, or a cationic surface active agent (For example, quarternary ammonium salt); — fluorochrome; — pH control agent; — defoaming agent; — lubricant; — antiseptics; — viscous amelioration agent; — coloring matter fixing agent; — waterproofing agent; — dispersant; — UV absorbent; — antifungal agent; — mordant; — antistatic-agent; — antioxidant; — a fluorescent brightener — The various known additives containing ** can also be contained. If required, a hardening agent can also be added to an ink absorbing layer.

[0025] In order to improve the adhesive property of the image recording layer to a base material,

before applying an image recording layer, a support surface may be applied to processing of corona discharge treatment etc. Furthermore, under-coating layers, such as a layer formed from a halogenation phenol or the vinyl chloride-vinyl acetate copolymer hydrolyzed partially, can be applied to a support surface, and the adhesive property of an image recording layer can be raised. When using an under-coating layer, as for the thickness, it is good that it is less than (desiccation coat thickness) 2 micrometers.

[0026] An image recording layer can exist in any amount effective in the purpose to mean. general — 2 — 46 g/m² — the good result is obtained if it exists preferably in the amount of 6 — 16 g/m² (respectively — 2—42 micrometers — desirable — the thickness of 6—15 micrometers — corresponding).

[Translation done.]

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- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

EXAMPLE

[Example] Practicality of this invention is clarified by the following examples.

:temperature which prepared the compound 2 of the synthetic above-mentioned of a compound 2 as follows was maintained below 40 degrees C, and the copper phthalocyanine (14g) was added to the chlorosulfonic acid (125g) over 45 minutes. And it heated at 140 degrees C – 150 degrees C of this mixture, and stirred for 5 hours. After cooling to a room temperature, the thionyl chloride (49g) was dropped over 30 minutes, and this mixture was maintained at 80 degrees C for 3 hours. After cooling to a room temperature, Hikami was filled with this mixture, it stirred with sufficient vigor, and temperature was maintained below 5 degrees C. Precipitate was carried out the ** exception, a lot of water washed at 5 degrees C, and it used at the following process. N and N-screw (hydroxyethyl) trimethylene diamine (27g) and a sodium carbonate (15g) were dissolved in water 500mL at 5 degrees C. The damp phthalocyanine filter cake was all added at once, and this reaction mixture was warmed to the room temperature, and was heated at 50 degrees C after that overnight. Ethanol (1.5L) was added and most organic substances were carried out the ** exception. Condensed the mixed liquor object, and it was made to deposit with an acetone, and carried out the ** exception, and the compound 2 was generated when it was made to wash and dry by ethanol. Other compounds and nickel analogs in Table I were also prepared similarly.

[0028] Example 1: copper-phthalocyanine coloring matter record element 1 fumed alumina (Cab-O-Sperse(trademark) PG003, Cabot Corp.), polyvinyl alcohol (Gohsenol(trademark) GH-23A, Nippon Gohsei Co., Ltd.) and 2, and 3-dihydroxy-1,4-dioxane (Clariant Corp.) was mixed by the ratio of 88:10:2, the aquosity coating formulation of 30 mass % solid content was obtained, and the coating solution for base layers was prepared. Fumed alumina (Cab-O-Sperse(trademark) PG003), polyvinyl alcohol (Gohsenol(trademark) GH-23A), and Polymer A were mixed by the ratio of 85:3:12, the aquosity coating formulation of 10 mass % solid content was obtained, and the coating solution for image acceptance layers was prepared. Polymer A is N-vinylbenzyl. – It is a mordant polymer containing the polymer particle which consists of N, N, and N-trimethyl ammonium-chloride 87 mass % and divinylbenzene 13 mass %. A fumed alumina particle has primary particle size with a diameter of 7–40nm, and is condensing it to a maximum of 150nm. Little addition of surfactant Zonyl(trademark) FSN (E. I du Pont de Nemours and Co.) and Olin (trademark)10G (Dixie chemical Co.) was carried out as a spreading assistant.

[0029] The bead coat of the above-mentioned coating solution was carried out to coincidence at 40 degrees C on the polyethylene coat paper base beforehand covered over corona discharge treatment. The coat of the image acceptance layer was carried out to the topmost part of a base layer. And this coating was dried at 60 degrees C by forced air, and the two-layer record element whose thickness of a bottom member and a topmost part layer is 40 micrometers (43 g/m²) and 2 micrometers (2.2 g/m²), respectively was produced.

[0030] : using the acceptance element of marketing of the following equipped with the record element 2 porosity image acceptance layer — Konica Photo Quality Ink Jet Paper Qp and No.KJP-LT-GH-15-QP PI.

[0031] It prepared using the deionized water which does a moisturizer, a diethylene glycol, and glycerol for the ink containing the coloring matter used for this invention of the preparation

above-mentioned of ink, and ink given in Table III, and does 0.5 mass % content of 0.003 mass % and a surfactant, and Surfynol 465 (trademark) (Air Products Co.) for six mass each %, a destruction-of-life agent, and ProxeGXL (trademark). These coloring matter concentrates were based on the solution absorption spectrum, and the last ink chose them so that the vitrification optical density of about 1.0 might be produced (when 1:1000 dilutes).

[0032] Although it was preparation metalization phthalocyanine dye of contrast ink, these ink as well as the ink of this invention was prepared except having used the following contrast coloring matter which has a different substituent from the above-mentioned thing of this invention.

C-1: direct — c is 2-4 in blue (Direct Blue) 199C-2:CuPc(SO₃Na) a(SO₂NH(CH₂)₃SO₃Na) bC-3:CuPc(SO₃Na) c and here.

(Pc and a are the same as what was specified by the above-mentioned formula)

[0033] The printing above-mentioned ink of a test image was filtered through 0.45-micrometer polytetrafluoroethylene filter, it put into empty Lexmark ink cartridge No.Lexmark 15MO120, and the ink station of Lexmark Z-51 printer was equipped. It consisted of four kinds of concentration patch magnitude of about 10x10mm, and the test image which is the range of the dot covering range of 25% – 100% was printed to the above-mentioned element 1 and Konica Photo Quality Ink Jet Paper QP, and No.KJP-LT-GH-15-QP PI.

[0034] About evaluation each ink of a test image, the status A red reflection density of the above-mentioned patch corresponding to 75% and 100% dot covering was measured using X-Rite (trademark) 820 densitometer. The red concentration of dot covering (D-max) is shown in Table III 100%. And the step image was placed for three days into the dark chamber which contains air and ozone gas 5ppm at 50% of relative humidity. The status A concentration of this step image was measured again, and the status A red concentration coloring matter retention in 75% dot covering patch was calculated about each ink. This also shows in Table III. It is thought that bigger retention than 45% can be admitted.

[0035]

[Table 3]

表III

| 色素含有インク | オゾン褪色保持率 (%) | |
|---------|--------------|--------|
| | 記録要素 1 | 記録要素 2 |
| 1 | 93 | 87 |
| 2 | 94 | 82 |
| 3 | 80 | NA |
| 4 | 82 | NA |
| 5 | 93 | 84 |
| C-1 | 24 | 23 |
| C-2 | 20 | 18 |
| C-3 | 20 | 19 |

[0036] The above-mentioned result shows that had less tenebrescence than contrast coloring matter in an ozone test, when the metalization phthalocyanine dye of this invention and a porous image acceptance layer are combined.

[0037] Example 2: this ink as well as the ink of this invention in Example 1 was prepared except having contained the preparation coloring matter 6 of the ink of nickel phthalocyanine dye this invention.

These ink as well as the ink of this invention was prepared except having used the following contrast coloring matter which has a different substituent from the above-mentioned thing of preparation this invention of contrast ink. C-4: A nickel (II) phthalocyanine tetra-sulfonic acid, 4 sodium salt (Aldrich Chemical Co.).

[0038] The above-mentioned ink was printed and evaluated like Example 1 only using printing of a test image, and the evaluation record element 1. The following result was obtained.

[0039]

[Table 4]

表IV

| 色素含有インク | オゾン褪色保持率(%) |
|---------|-------------|
| 6 | 100 |
| C-4 | 44 |

[0040] The above-mentioned result shows that there was no tenebrescence in an ozone test as compared with contrast coloring matter, when the metalization phthalocyanine dye of this invention and a porous image acceptance layer are combined.

[Translation done.]

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(71)出願人 590000846

イーストマン コダック カンパニー
アメリカ合衆国, ニューヨーク14650, 口
チェスター, ステイト ストリート343

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(72)発明者 アンドレイ アンドリーブスキ
アメリカ合衆国, ニューヨーク 14580,
ウェブスター, マジエスティック ウェイ
1232

(31)優先権主張番号 09/813760

(74)代理人 100077517

(32)優先日 平成13年3月21日 (2001.3.21)

弁理士 石田 敏 (外5名)

(33)優先権主張国 米国 (US)

最終頁に続く

(54)【発明の名称】 インクジェット印刷方法

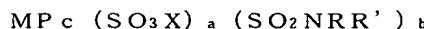
(57)【要約】

【課題】 像のオゾン安定性を向上させるインクジェット印刷方法を提供する。

【解決手段】 a)連続したボイドを有する多孔性画像受容層を上に有する支持体を含んで成るインクジェット記録要素を用意し、b)前記画像受容層の上に、水、保湿剤、及び金属化フタロシアニン色素を含む液体インクの小滴を像様に適用するインクジェット印刷方法。前記色素は次式: MPc(SO₃X)_a(SO₂NRR')_b である。Mは金属、Pcはフタロシアニン核、Xは水素、アルカリ金属又は有機カチオン、aは0~2、Rは水素、炭素数1~15の置換もしくは非置換のアルキル基、置換もしくは非置換のアリール基、又は置換もしくは非置換の複素環式基、R'はヒドロキシ基を有する炭素数1~15の置換もしくは非置換のアルキル基、ヒドロキシ基を有する置換もしくは非置換のアリール基、又はヒドロキシ基を有する置換もしくは非置換の複素環式基、bは1~4であるが、a+bが平均して3~4である)。

【特許請求の範囲】

【請求項1】 a) 連続したボイドを有する多孔性画像受容層を上に有する支持体を含んで成るインクジェット記録要素を用意する工程、そして
 b) 前記画像受容層の上に、水、保湿剤、及び金属化フタロシアニン色素を含む液体インクの小滴を像様に適用する工程を有するインクジェット画像のオゾン安定性を向上させるためのインクジェット印刷方法であって、前記金属化フタロシアニン色素が次式を有するインクジェット印刷方法：



(上式中、

Mは、金属であり、

Pcは、フタロシアニン核であり、

Xは、水素、アルカリ金属又は有機カチオンであり、

aは、0～2であり、

Rは、水素、炭素数1～15の置換もしくは非置換のアルキル基、置換もしくは非置換のアリール基、又は置換もしくは非置換の複素環式基であり、

R'は、ヒドロキシ基を有する炭素数1～15の置換もしくは非置換のアルキル基、ヒドロキシ基を有する置換もしくは非置換のアリール基、又はヒドロキシ基を有する置換もしくは非置換の複素環式基であり、そしてbは、1～4であるが、a+bが平均して3～4である)。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明はインクジェット画像のオゾン安定性を向上させるインクジェット印刷方法に関する。

【0002】

【従来の技術】インクジェット印刷はデジタル信号に応答して画像記録要素にピクセル毎の様式でインク液滴を付着させることによって画像を形成するノンインパクト方法である。画像記録要素上へのインク液滴の付着を制御して、所望の画像を生成するのに用いることができる種々の方法が存在する。一つのプロセスは、コンティニュアスインクジェットとして知られており、液滴の連続ストリームを帶電させ、画像記録要素の表面上へと像様に偏向させるが、画像形成されない液滴は捕捉されインク溜に戻される。もう一つのプロセスは、ドロップオンデマンドインクジェットとして知られており、個々のインク液滴を必要なときに画像記録要素上に放出して所望の画像を形成する。ドロップオンデマンド印刷で、インク液滴の放出を制御する一般的な方法には、圧電変換器及び熱バブル形成が含まれる。インクジェットプリンタは、工業用ラベリングから事務文書の少量印刷及びピクトリアル画像形成の範囲のマーケットにわたる広範囲の用途を有している。

【0003】種々のインクジェットプリンタに用いられ

るインクは、色素系もしくは顔料系に分類される。色素は、キャリア媒体に溶解される色材である。キャリア媒体は、室温で液体又は固体となることができる。通常使用されるキャリア媒体には、水、又は水と有機補助溶剤との混合物が含まれる。個々の色素分子はキャリア媒体の分子によって囲まれている。色素系インクの場合、顕微鏡下で見られる粒子は無い。色素系インクジェットインクの技術分野では最近多くの進歩が見られるが、そのようなインクはなおも、例えば、普通紙において低光学濃度であり、耐光性が劣るといったような欠点を有している。キャリア媒体として水を用いる場合、一般的に、そのようなインクは耐水性も劣るという欠点も有する。

【0004】上記インクを用いることができるインクジェット受容要素は、水に短時間さらしたときに、スマア(smear)、ブリード、又はワンダー(wander)しない高濃度画像を生成することを含めたいくつかの要件に適合しなければならない。

【0005】米国特許第4,632,703号、同第6,149,722号及び同第6,015,896号、国際公開公報W000/08103号同第W098/4923号は、インクジェット印刷に使用するフタロシアニン色素を含有するインクに関する。しかし、これらの文献には、これらのインクが多孔性画像受容層を有する記録要素に関して有用であるとの記載はない。

【0006】

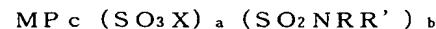
【発明が解決しようとする課題】インクジェット画像のオゾン安定性を向上させるインクジェット印刷方法を提供することが本発明の目的である。

【0007】

【課題を解決するための手段】上記の目的を

a) 連続したボイドを有する多孔性画像受容層を上に有する支持体を含んで成るインクジェット記録要素を用意する工程、そして

b) 前記画像受容層の上に、水、保湿剤、及び金属化フタロシアニン色素を含む液体インクの小滴を像様に適用する工程を有するインクジェット画像のオゾン安定性を向上させるためのインクジェット印刷方法であって、前記金属化フタロシアニン色素が次式：

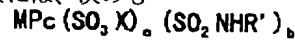


(上式中、Mは、金属であり、Pcは、フタロシアニン核であり、Xは、水素、アルカリ金属又は有機カチオンであり、aは、0～2であり、Rは、水素、炭素数1～15の置換もしくは非置換のアルキル基、置換もしくは非置換のアリール基、又は置換もしくは非置換の複素環式基であり、R'は、ヒドロキシ基を有する炭素数1～15の置換もしくは非置換のアルキル基、ヒドロキシ基を有する置換もしくは非置換のアリール基、又はヒドロキシ基を有する置換もしくは非置換の複素環式基であり、そしてbは、1～4であるが、a+bが平均して3～4である) を有するインクジェット印刷方法を提供する本発明に従って達成する。上記化合物を用いるとイン

クジェット画像のオゾン安定性が向上した。

【0008】

【発明の実施の形態】本発明の好ましい態様では、用い
ることができる金属化フタロシアニン色素には、次のも



(MはCuであり、そしてX、Pc、a及びbは前出の通りである)

のが含まれる:

【0009】

【表1】

| 色素 | R' |
|----|-------------------------------------|
| 1 | |
| 2 | |
| 3 | |
| 4 | -CH ₂ CH ₂ OH |

【0010】

【表2】
 $MPc(SO_3X)_a(SO_2NRR')_b$

(R=R'=-CH₂CH₂OH、そしてX、Pc、a及びbは前出の通りである)

表II

| 色素 | M |
|----|----|
| 5 | Cu |
| 6 | Ni |

【0011】本発明の別の好ましい態様では、Rはヒドロキシ基を有する炭素数1～15の置換もしくは非置換のアルキル基、ヒドロキシ基を有するアリール基又はヒドロキシ基を有する複素環式置換基である。

【0012】上記色素は意図した目的に有効ないかなる量でも用いることができる。一般的に、インクジェットインク組成物の0.2～5質量%、好ましくは0.3～3質量%の量で色素が存在する場合に、良好な結果が得られた。また、色素混合物も用いることができる。

【0013】本発明に用いられるインクジェット記録要素の支持体はインクジェット受容体に通常用いられるもの、例えば、紙、樹脂コート紙、ポリエチレンテレフタレートのようなポリエステルタイプの樹脂等のプラスチック、ポリカーボネート樹脂、ポリスルホン樹脂、メタクリル樹脂、セロファン、アセテートプラスチック、二

酢酸セルロース、三酢酸セルロース、塩化ビニル樹脂、ポリエチレンナフタレン、二酢酸ポリエステル、種々のガラス材料、並びに米国特許出願第09/656,129号（2000年8月29日出願）明細書に記載されているミクロボイド

40 ポリエステル、商品名Teslin（商標）(PPG Industries, Inc., ピツツバーグ、ペンシルバニア)で販売されているポリエチレンポリマー含有材料、Tyvek（商標）合成紙(DuPont Corp.)、及びOppalyte（商標）フィルム(Mobil Chemical Co.)等の微多孔性材料並びに米国特許第5,244,861号明細書に記載されているような他の複合フィルム等となることができる。本発明に用いる支持体は、例えば、1.2～50.0 μm、好ましくは、7.5～30.0 μmの厚みを有することができる。

【0014】必要ならば、酸化防止剤、帶電防止剤、可塑剤及び他の既知の添加物を支持体中に導入してもよ

い。好ましい態様では、紙を用いる。

【0015】本発明の好ましい態様では、多孔性インク受容層は、シリカ、アルミナ、二酸化チタン、クレイ、炭酸カルシウム、硫酸バリウム、又は酸化亜鉛等の無機粒子を含有する。別の好ましい態様では、多孔性インク受容層は、無機粒子30%～95%及びポリマーバインダー（例えば、ゼラチン、ポリビニルアルコール、ポリビニルピロジノン、又はポリ酢酸ビニル）5%～70%を含む。また多孔性インク受容層は、有機ビーズを有するか、又は米国特許第5,374,475号及び同第4,954,395号明細書に示されるような無機フィラー粒子を含まないポリマー微孔性構造を有することもできる。

【0016】画像受容層に用いることができるバインダーの例には、ポリビニルアルコール、ポリビニルピロジドン、ポリエチルオキソゾリン、脱イオン化されているか、脱イオン化されていないタイプIVの骨ゼラチン、酸処理オセインゼラチン又は豚皮ゼラチンが含まれる。親水性ポリマーは、0.4～30g/m²、好ましくは1～16g/m²の量で存在することができる。

【0017】本発明の水性インク組成物のpHを、有機又は無機の酸もしくは塩基を添加することによって調節することができる。有用なインクは、使用する色素の種類に依存して、2～7の好ましいpHを有することができる。典型的な無機酸には、塩酸、リン酸及び硫酸が含まれる。典型的な有機酸には、メタンスルホン酸、酢酸及び乳酸が含まれる。典型的な無機塩基には、アルカリ金属水酸化物及び炭酸塩が含まれる。典型的な有機塩基には、アンモニア、トリエタノールアミン及びテトラメチルエチレンジアミンが含まれる。

【0018】プリントヘッドのオリフィス内でインクが乾燥するか、固まりつくのを防止するために、本発明のインクジェットインク組成物に保湿剤を用いる。使用できる保湿剤の例には、多価アルコール、例えば、エチレングリコール、ジエチレングリコール、トリエチレングリコール、プロピレングリコール、テトラエチレングリコール、ポリエチレングリコール、グリセロール、2-メチル-2,4-ペンタンジオール、1,2,6-ヘキサントリオール及びチオグリコール；アルキレングリコールから誘導される低級アルキルモノ又はジエーテル、例えば、エチレングルコールモノメチル又はモノエチルエーテル、ジエチレングリコールモノメチル又はモノエチルエーテル、トリエチレングリコールモノメチル又はモノエチルエーテル、ジエチレングリコールジメチル又はジエチルエーテル、及びジエチレングリコールモノブチルエーテル；窒素含有環状化合物、例えば、ピロリドン、N-メチル-2-ピロリドン及び1,3-ジメチル-2-イミダゾリジノン；並びにイオウ含有化合物、例えば、ジメチルスルホキシド及びテトラメチレンスルホンが含まれる。本発明の組成物に好ましい保湿剤

は、ジエチレングリコール、グリセロール、又はジエチレングリコールモノブチルエーテルである。

【0019】受容基体、特に基体が高度サイズ紙の場合にインク浸透を助けるために、本発明の水性インクに水混和性有機溶媒を添加してもよい。そのような溶媒の例には、アルコール類、例えば、メチルアルコール、エチルアルコール、n-ブロピルアルコール、イソブロピルアルコール、n-ブチルアルコール、sec-ブチルアルコール、t-ブチルアルコール、イソブチルアルコール、フルフリルアルコール、及びテトラヒドロフルフリルアルコール；ケトン類もしくはケトアルコール類、例えば、アセトン、メチルエチルケトン及びジアセトンアルコール；エーテル類、例えば、テトラヒドロフラン及びジオキサン；並びにエステル類、例えば、乳酸エチル、エチレンカーボネート及びプロピレンカーボネートが含まれる。

【0020】界面活性剤を添加して紙に対するインクの表面張力を適当なレベルに調節してもよい。界面活性剤は、アニオン性、カチオン性、両性もしくは非イオン性となることができる。本発明のインク組成物に好ましい界面活性剤は、最終濃度で0.1%～1.0%のSurfynols（商標）（Air Products製）である。

【0021】水性インク中での微生物、例えば、カビ、真菌類の成長を抑制するために、本発明の組成物に殺生剤を添加してもよい。本発明のインク組成物に好ましい殺生剤は、最終濃度0.05～0.5質量%のProxel（商標）GXL（Zeneca Specialties Co.）である。

【0022】本発明の典型的なインク組成物は、例えば以下のもの（質量基準）となることができる：色材（0.2～5%）、水（20～95%）、保湿剤（5～70%）、水混和性補助溶媒（2～20%）、界面活性剤（0.1～10%）、殺生剤（0.05～5%）、及びpH調節剤（0.1～10%）。

【0023】本発明のインクジェットインク組成物中に随意選択的に存在することができる追加の添加物には、増粘剤、導電性強化剤、コーティング防止剤、乾燥剤、及び消泡剤が含まれる。

【0024】本発明の記録要素に用いられる画像記録層は、本発明に用いられる記録要素の非プロッキング特性に寄与し、それらの耐汚染性をコントロールするための、艶消し剤、例えば、二酸化チタン、酸化亜鉛、シリカ及びポリマービーズ（例えば、架橋ポリメチルメタクリレートもしくはポリスチレンビーズ）；インク吸収性樹脂もしくは層のエージング挙動を改善するため、そこに連続適用されるインクの吸収促進及び乾燥のため、インク受容層の表面均一性を高めるため、そして乾燥コーティングの表面張力を調節するための、界面活性剤、例えば、非イオン性、炭化水素もしくはフッ化炭素界面活性剤又はカチオン性界面活性剤（例えば、第四級アンモニウム塩）；蛍光色素；pHコントロール剤；消泡剤；

滑剤；防腐剤；粘性改良剤；色素定着剤；防水剤；分散剤；UV吸収剤；防かび剤；媒染剤；帯電防止剤；酸化防止剤；蛍光増白剤、等を含む種々の既知の添加剤も含有することができる。必要ならば、硬膜剤もインク受容層に添加することができる。

【0025】支持体に対する画像記録層の接着性を改善するために、画像記録層を適用する前に、支持体表面をコロナ放電処理等の処理にかけてもよい。さらに、ハログン化フェノール又は部分的に加水分解された塩化ビニル-酢酸ビニルコポリマーから形成される層等の下引き層を支持体表面に適用して、画像記録層の接着性を高めることができる。下引き層を使用する場合は、その厚みは2μm未満（乾燥コート厚）であるのがよい。

【0026】画像記録層は意図する目的に有効ないずれの量でも存在することができる。一般的に2～46g/m²、好ましくは6～16g/m²（それぞれ、2～42μm、好ましくは6～15μmの厚みの相当する）の量で存在すると良好な結果が得られている。

【0027】

【実施例】以下の例によって本発明の実用性を明らかにする。

化合物2の合成

前述の化合物2を次のように調製した：温度を40℃より下に維持して、銅フタロシアニン（14g）を45分かけてクロロスルホン酸（125g）に添加した。そして、この混合物140℃～150℃に加熱し、5時間攪拌した。室温まで冷却した後、塩化チオニル（49g）を30分かけて滴下し、この混合物を3時間80℃に維持した。室温まで冷却した後、この混合物を氷上に注ぎ、勢いよく攪拌し、温度を5℃より下に維持した。沈殿を濾別し、5℃で大量の水で洗浄し、次の工程で用いた。N,N-ビス（ヒドロキシエチル）トリメチレンジアミン（27g）及び炭酸ナトリウム（15g）を、5℃で水500mLに溶解させた。湿ったフタロシアニンフィルターを一度に全部加え、この反応混合物を室温まで温め、その後50℃で一晩加熱した。エタノール（1.5L）を加え、大部分の有機物質を濾別した。混合液体を濃縮し、アセトンで析出させ、濾別しエタノールで洗浄して、乾燥せると化合物2を生成した。表I中の他の化合物及びニッケル類似体も同様にして調製した。

【0028】例1：銅フタロシアニン色素

記録要素1

ヒュームドアルミナ（Cab-O-Sperse（商標）PG003、Cabot Corp.）、ポリビニルアルコール（Gohsenol（商標）GH-23A、Nippon Gohsei Co., Ltd.）及び2,3-ジヒドロキシ-1,4-ジオキサン（Clariant Corp.）を88:10:2の比率で混合して、30質量%固形分の水性コーティング調合物を得て、ベース層用のコーティング溶液を調製した。ヒュームドアルミナ（Cab-O-Sperse

（商標）PG003）、ポリビニルアルコール（Gohsenol（商標）GH-23A）及びポリマーAを85:3:12の比率で混合して、10質量%固形分の水性コーティング調合物を得て、画像受容層用のコーティング溶液を調製した。ポリマーAは、N-ビニルベンジル-N,N,N-トリメチル塩化アンモニウム87質量%及びジビニルベンゼン13質量%からなるポリマー粒子を含む媒染剤ポリマーである。ヒュームドアルミナ粒子は直径7～40nmの一次粒径を有し、最大150nmまで凝集している。界面活性剤Zonyl（商標）FSN（E.I. du Pont de Nemours and Co.）及びOlin（商標）10G（Dixie chemical Co.）を塗布助剤として少量添加した。

【0029】上記コーティング溶液を、前もってコロナ放電処理にかけたポリエチレンコート紙ベース上に40℃で同時にビードコートした。画像受容層をベース層の最上部にコートした。そして、このコーティングを強制空気で60℃で乾燥して、底部層と最上部層との厚みがそれぞれ40μm（43g/m²）及び2μm（2.2g/m²）である2層記録要素を作製した。

【0030】記録要素2

多孔性画像受容層を備えた以下の市販の受容要素を用いた：Konica Photo Quality Ink Jet Paper QP, No. KJP-LT-GH-15-QP PI。

【0031】インクの調製

前述の本発明に用いる色素を含有するインク及び表II-Iに記載のインクを、保湿剤、ジェチレングリコール及びグリセロールを各6質量%、殺生剤、ProxelGX（商標）を0.003質量%、及び界面活性剤、Surfynol 465（商標）（Air Products Co.）を0.5質量%含有する脱イオン水を用いて調製した。これらの色素濃縮物は溶液吸收スペクトルに基づいており、最終インク（1:1000に希釈されたとき）が、約1.0の透化光学濃度を生じるように選択した。

【0032】対照インクの調製

金属化フタロシアニン色素ではあるが、本発明の前述のものとは異なる置換基を有する次の対照色素を用いた以外は、本発明のインクと同様にこれらのインクを調製した。

C-1：ダイレクトブルー（Direct Blue）199
C-2：CuPc (SO_3Na)_a ($\text{SO}_2\text{NH}(\text{CH}_2)_3\text{SO}_3\text{Na}$)_b
C-3：CuPc (SO_3Na)_c、ここでcは2～4である。

（Pc及びaは、前出の式で規定したものと同じである）

【0033】テスト画像の印刷

上記インクを0.45μmポリテトラフルオロエチレンフィルターを通して濾過し、空のLexmarkインクカートリッジNo. Lexmark 15M0120にいれ、Lexmark Z-51プリンタのインクステーションに装着した。4種類の濃度パ

ツチ大きさ約10×10mmからなり、ドット被覆範囲25%～100%の範囲であるテスト画像を、上述の要素1及びKonica Photo Quality Ink Jet Paper QP、No. KJP-LT-GH-15-QP PIに印刷した。

【0034】テスト画像の評価

各インクについて、75%及び100%ドット被覆に対応する上記パッチのステータスA赤反射濃度を、X-Rite(商標)820デシントメーターを用いて測定した。100%ドット被覆(D-max)の赤濃度を表IIIに示す。

表III

| 色素含有インク | オゾン褪色保持率(%) | |
|---------|-------------|-------|
| | 記録要素1 | 記録要素2 |
| 1 | 93 | 87 |
| 2 | 94 | 82 |
| 3 | 80 | NA |
| 4 | 92 | NA |
| 5 | 93 | 84 |
| C-1 | 24 | 23 |
| C-2 | 20 | 18 |
| C-3 | 20 | 19 |

【0036】上記結果は、本発明の金属化フタロシアニン色素と多孔性画像受容層とを組み合わせると、オゾンテストにおいて、対照色素よりも褪色が少なかったことを示す。

【0037】例2：ニッケルフタロシアニン色素 本発明のインクの調製

色素6を含有していた以外は、例1での本発明のインクと同様にこのインクを調製した。

対照インクの調製

本発明の前述のものとは異なる置換基を有する次の対照色素を用いた以外は、本発明のインクと同様にこれらのインクを調製した。C-4：ニッケル(II)フタロシアニンテトラスルホン酸、四ナトリウム塩(Aldrich Chemical Co.)。

【0038】テスト画像の印刷と評価

フロントページの続き

(51)Int.Cl.⁷
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そして、ステップ画像を、相対湿度50%で空気とオゾンガス5ppmを含有する暗チャンバー内に3日間置いた。このステップ画像のステータスA濃度を再測定し、75%ドット被覆パッチの場合のステータスA赤濃度色素保持率を各インクについて計算した。これも表IIIに示す。45%より大きな保持率が認めできると考えられる。

【0035】

表3

記録要素1だけを用いて例1と同様に上記インクを印刷し、評価した。次の結果が得られた。

【0039】

表4

表IV

| 色素含有インク | オゾン褪色保持率(%) |
|---------|-------------|
| 6 | 100 |
| C-4 | 44 |

【0040】上記結果は、本発明の金属化フタロシアニン色素と多孔性画像受容層とを組み合わせると、オゾンテストにおいて、対照色素と比較して褪色がなかったことを示す。

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(72)発明者 ヘルムト ウェバー
アメリカ合衆国、ニューヨーク 14580,
ウェブスター、マリゴールド ドライブ
1089

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